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(54) **Deposition of gamma-AL₂O₃ by means of CVD**

(57) There is disclosed a coated body having as the outer layer a layer of γ -Al₂O₃ deposited by chemical vapor deposition, preferably at a temperature of from 700-900°C.

The γ -Al₂O₃ layer is formed through the use of a gaseous mixture including H₂S in amounts significantly higher than those presently used and at a temperature of from 700-900°C. The method is also disclosed.

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Description

BACKGROUND OF THE INVENTION

- 5 [0001] Aluminum oxide (alumina, Al_2O_3) exists in many metastable polymorphs such as γ , η , θ , δ , κ , and χ in addition to the thermodynamically stable α - Al_2O_3 phase (corundum). When produced by chemical vapor deposition (CVD), Al_2O_3 crystallizes into κ - Al_2O_3 and θ - Al_2O_3 modifications in addition to the stable α - Al_2O_3 . Earlier CVD coatings were usually mixtures of several polymorphs, the most commonly occurring metastable Al_2O_3 modification being κ - Al_2O_3 . Today, both α - Al_2O_3 and κ - Al_2O_3 polymorphs are used as hard coatings, and they can be deposited in a controlled way by modern CVD technology shown, for example in U.S. Patents 5,137,774 and 5,700,569.
- 10 [0002] Dopants of hydrogen sulfide (H_2S), phosphorus chloride (PCl_3) carbonoxysulfide (COS) or phosphine (PH_3) can be applied in order to increase the growth rate and thickness uniformity of the alumina layers. The most commonly applied dopant is H_2S as also disclosed in U.S. Patent 4,619,886. While amounts of H_2S in the total CVD gaseous mixture of from 0.003 to 1% by volume and temperatures of 700 to 1200°C are broadly disclosed in that patent, all exemplifications of the process therein are below 0.5 vol % and generally around 0.1 to 0.3 vol % H_2S used at temperatures of 1000-1030°C. H_2S has been called the "magical dopant" in view of its effect on improving the growth rate and uniformity of Al_2O_3 coatings applied by conventional CVD techniques at temperatures around 980°C. See, Oshika et al., "Unveiling the Magic of H_2S on the CVD- Al_2O_3 Coating", J. Phys IV France 9 (1999), Pr 8-877-Pr 8-883.
- 15 [0003] CVD κ - Al_2O_3 is considered to exhibit morphological advantages (smaller grain size and lower porosity), lower thermal conductivity and even a higher hardness when compared with the CVD α - Al_2O_3 phase. These are important properties when metal cutting is concerned. However, at the relatively high temperatures (> 1000°C) reached during metal cutting, metastable κ - Al_2O_3 may transform to the stable α - Al_2O_3 polymorph. γ - Al_2O_3 , when deposited using physical vapor deposition (PVD) or plasma assisted CVD has been found to exhibit high hardness and good wear properties. See, for example, WO 9924634 and U.S. Patent No. 5,879,823. However, γ - Al_2O_3 has not been available using conventional CVD techniques.
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OBJECTS AND SUMMARY OF THE INVENTION

- [0004] It is an object of this invention to avoid or alleviate the problems of the prior art.
- 30 [0005] It is further an object of this invention to provide γ - Al_2O_3 using conventional CVD.
- [0006] In one aspect of the invention there is provided a coated body having as the outer layer, a layer of γ - Al_2O_3 deposited by chemical vapor deposition.
- [0007] In another aspect of the invention there is provided a method of forming a coated body having a layer of γ - Al_2O_3 comprising coating the body with a gaseous mixture of AlCl_3 , CO_2 , H_2 and H_2S at a temperature of from about 35 600 to 800°C, the H_2S being present in amounts of at least 0.7% of the total mixture.

BRIEF DESCRIPTION OF THE DRAWINGS

- 40 [0008] The Figure is a graph of growth rates of κ and γ - Al_2O_3 at varying temperatures and amounts of H_2S in the gaseous coating mixture.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

- 45 [0009] It has hitherto been thought that γ - Al_2O_3 can only be obtained by plasma assisted CVD or PVD processes. It has now surprisingly been found that γ - Al_2O_3 can be obtained by using conventional CVD under specific circumstances discussed below.
- [0010] Growth rates of α -alumina vs. H_2S content at 1000°C and 800°C are shown in The Figure. An important observation is that at 800°C, reasonably high growth rates could be obtained. The most important observation, however, is that at higher H_2S contents, γ - Al_2O_3 was obtained. At 800°C γ - Al_2O_3 could be obtained at H_2S contents of 0.75-1.7% by volume of the total gaseous mixture, preferably greater than 1 vol %, and at a pressure of 100 mbar. At 1000°C, regardless of the amounts of H_2S , κ - Al_2O_3 is always formed. Thus, by carefully controlling the amount of H_2S and the temperature of the application, the preferred polymorph, γ -alumina, can surprisingly be formed. When studied using TEM (transmission electron microscopy), γ - Al_2O_3 exhibited a very high defect density and obviously a high hardness.
- 50 [0011] The product of the present invention may be made utilizing conventional CVD techniques and apparatus, using, however, a greater amount of H_2S than conventionally used in CVD processes and a higher pressure. H_2S is added in amounts greater than 0.7 vol %, generally 0.75 to 1.7 vol %, preferably greater than 1 up to about 1.5 vol %, of the total gaseous mixture. The amounts of the other reactants can be adjusted accordingly but usually the alumina formers, an aluminum halide and an oxidizing gas (e.g., water vapor formed by the reaction of CO_2 and/or CO and H_2)
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are maintained as before and the amount of reducing agent (excess H_2) is reduced.

[0012] The coating process is performed at temperatures of from about 700 to 900°C, preferably 750 to 850°C, at a pressure of from about 50 to 600 mbar, preferably from about 100 to 300 mbar, for a time sufficient to form the coating, generally from about 2 to 10 hours, preferably from about 4 to 8 hours.

[0013] The resulting coating is from about 1.0 to 5 μm , preferably from about 2 to 4 μm , in thickness.

[0014] The body on which the $\gamma-Al_2O_3$ layer is applied can be a cemented carbide, ceramic, cermet (for metal cutting purposes) or steel (for catalysis). These bodies are well-known in the art and any such conventional material may be used.

[0015] The $\gamma-Al_2O_3$ layer may be applied as the outermost or as an inner layer. When used as the outermost layer, the $\gamma-Al_2O_3$ layer may be applied onto an Al_2O_3 layer, which itself can be applied onto one or more other layers such as, for example, TiC and (Ti,Al)N. The Al_2O_3 layer can be an alpha phase, a kappa phase or a mixture of alpha and kappa phase Al_2O_3 . The $\gamma-Al_2O_3$ layer may also be applied onto a TiN, Ti(C,N) or (Ti,Al)N layer.

[0016] Similarly, when the $\gamma-Al_2O_3$ layer is applied as an inner layer, there may be other layers such as Al_2O_3 , TiC, Ti(C,N), TiN or the like applied atop the $\gamma-Al_2O_3$ layer.

[0017] These various inner and or outer layers may be applied by CVD, MTCVD or PVD.

[0018] The invention is additionally illustrated in connection with the following Examples which are to be considered as illustrative of the present invention. It should be understood, however, that the invention is not limited to the specific details of the Examples.

Example 1

[0019] A single layer of $\gamma-Al_2O_3$ was deposited using the following process data on a Ti(C,N) layer having a thickness of 3 μm :

T = 800°C

H_2S = 1%

$AlCl_3$ = 2.5%

CO_2 = 5.0%

H_2 = balance

Pressure (P) = 100 mbar

Deposition time is 6 hours

[0020] A coating composed of $\gamma-Al_2O_3$ was obtained. The same coating was also deposited atop PVD TiN, Ti(C,N) and (Ti,Al)N layers with a thickness of 3 μm . Further, CVD coatings of $\kappa-Al_2O_3$ and $\alpha-Al_2O_3$ were deposited on the PVD layers as well as CVD layers for comparative tests dealt with later on.

Hardness of $\gamma-Al_2O_3$:

[0021]

Alumina Phase	Hardness
$\gamma-Al_2O_3$	23 GPa
$\alpha-Al_2O_3$	20 GPa
$\kappa-Al_2O_3$	21 GPa

Orientation Relationships

[0022] The single layers of $\gamma-Al_2O_3$ were deposited using the following process data on a PVD TiN, Ti(C,N) and (Ti,Al)N layers having a thickness of 3 μm :

T = 700°C

H_2S = 1.6%

$AlCl_3$ = 2.5%

CO_2 = 7.0%

H_2 = balance

P = 100 mbar

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Deposition time is 8 hours

TEM micrographs of the PVD TiN- γ -Al₂O₃ interface confirmed the following orientation relationship between PVD TiN and γ -Al₂O₃:

$$\begin{aligned} (111)_{\text{PVD-TiN}} // (111)_{\gamma} \\ [\bar{1}\bar{1}0]_{\text{PVD-TiN}} // [\bar{1}\bar{1}0]_{\gamma} \end{aligned}$$

[0023] This orientation relationship is valid for γ -Al₂O₃-PVD TiN, Ti(C,N) or (Ti,Al)N in general and is naturally not dependent on which technique (PVD or CVD) is used to deposit γ -Al₂O₃. The orientation relationship describes in general epitaxy between a face-centered cubic (fcc, preferably fcc B1) coating (TiN, Ti(C,N), (Ti,Al)N) and γ -Al₂O₃ (cubic spinel structure).

[0024] Cutting performance in turning of Stainless Steel 1672:

Cutting Speed: 200 m/min
Feed: 0.4 mm/r
Depth of Cut: 2.0 mm
Insert Style: CNMG 120408-M3
Coolant: No

Coating (thickness 3 μ m on TiCN coating)	Average life time/min
γ -Al ₂ O ₃	9.8
α -Al ₂ O ₃	6.5
κ -Al ₂ O ₃	9.6

[0025] Edge strength /chipping resistance of alumina polymorphs
Turning against shoulder

Cutting Speed: 200 m/min
Feed: 0.4 mm/r
Depth of Cut: 2.0 mm
Insert Style: CNMG 120408-M3
Coolant: No

Coating (thickness 3 μ m on TiCN + 3 μ m Al ₂ O ₃)	Edge chipping after 2 min
γ -Al ₂ O ₃	10%
α -Al ₂ O ₃	15%
κ -Al ₂ O ₃	10%

[0026] Edge strength/chipping resistance in milling SS2244

[0027] The chipping resistance of PVD TiN, Ti(C,N) and (Ti,Al)N coatings with and without an alumina top layer were studied.

Cutting Speed: 220 m/min
Feed: 0.2 mm/tooth
Depth of Cut: 2.5 mm
Insert Style: SEKN1203

Coating	Thickness	Chipping after 600 mm	Performance/mm
PVD TiN	3	5%	3660
PVD Ti(C,N)	3	5%	4200

(continued)

Coating	Thickness	Chipping after 600 mm	Performance/mm
PVD (Ti,Al)N	3	5%	4600
PVD TiN	6	10%	4700
PVD Ti(C,N)	6	10%	5100
PVD (Ti,Al)N	6	10%	6800
PVD Ti(C,N)- γ -Al ₂ O ₃	3+3	10%	7200
PVD Ti(C,N)- α -Al ₂ O ₃	3+3	30%	7100
PVD Ti(C,N)- κ -Al ₂ O ₃	3+3	25%	5100

[0028] It is obvious that γ -Al₂O₃ which can be deposited at lower temperatures than the other CVD alumina phases did not anneal out the compressive stresses in the PVD layers resulting in the better edge strength.

[0029] The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

Claims

1. A coated body having as the outer layer, a layer of γ -Al₂O₃ deposited by chemical vapor deposition.
2. The coated body of claim 1 wherein the γ -Al₂O₃ layer is deposited at a temperature of from about 700 to 900°C.
3. The coated body of claim 1 wherein the γ -Al₂O₃ layer is deposited on one or more layers taken from the group consisting of TiC, TiN, Ti(C,N), (Ti,Al)N and Al₂O₃.
4. The coated body of claim 3 wherein the γ -Al₂O₃ layer is deposited upon one or more layers of α -Al₂O₃, κ -Al₂O₃ or mixtures thereof.
5. The coated body of claim 3 wherein the γ -Al₂O₃ layer is deposited upon a (Ti,Al)N layer.
6. The coated body of claim 1 wherein the γ -Al₂O₃ layer is deposited on a layer which has been deposited by physical vapor deposition.
7. The coated body of claim 6 wherein the γ -Al₂O₃ is deposited on one or more of TiC, TiN, Ti(C,N) and (Ti,Al)N.
8. The coated body of claim 1 wherein the γ -Al₂O₃ is deposited on a layer having a face-centered cubic structure.
9. The coated body of claim 8 wherein the γ -Al₂O₃ has an orientation relationship with the layer having a face-centered cubic structure (fcc) of

$$\begin{aligned} (111)_{\text{PVD-fcc}} // (111)_{\gamma} \\ [\bar{1}\bar{1}0]_{\text{PVD-fcc}} // [\bar{1}\bar{1}0]_{\gamma} \end{aligned}$$
10. The coated body of claim 9 wherein the layer having a face-centered cubic structure is taken from the group consisting of TiN, TiC, Ti(C,N), (Ti,Al)N and mixtures thereof.
11. The coated body of claim 10 wherein the layer having a face-centered cubic structure is a fcc B1 structure deposited by CVD technique.
12. The coated body of claim 10 wherein the layer having a face-centered cubic structure is a fcc B1 structure deposited by PVD technique.

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13. The coated body of claim 1 wherein the body is composed of a cemented carbide, cermet, ceramic or steel.
14. The coated body of claim 13 wherein the body is a cemented carbide.
- 5 15. A method of forming a coated body having a layer of $\gamma\text{-Al}_2\text{O}_3$ comprising coating the body with a gaseous mixture of AlCl_3 , CO_2 , H_2 and H_2S at a temperature of from about 700 to 900°C, the H_2S being present in amounts of at least 0.7% of the total mixture.
- 10 16. The method of claim 15 wherein the coating is conducted at a temperature of from about 750 to 850°C.
17. The method of claim 15 wherein the coating is conducted at a pressure of from about 100 to 500 mbar.
18. The method of claim 15 wherein the body being coated is a ceramic, cermet, cemented carbide or steel.
- 15 19. The method of claim 18 wherein the body being coated contains at least one other layer of TiC , TiN , $\text{Ti}(\text{C,N})$, TiAlN or Al_2O_3 .
20. The method of claim 19 wherein the said other layer is applied by physical vapor deposition.

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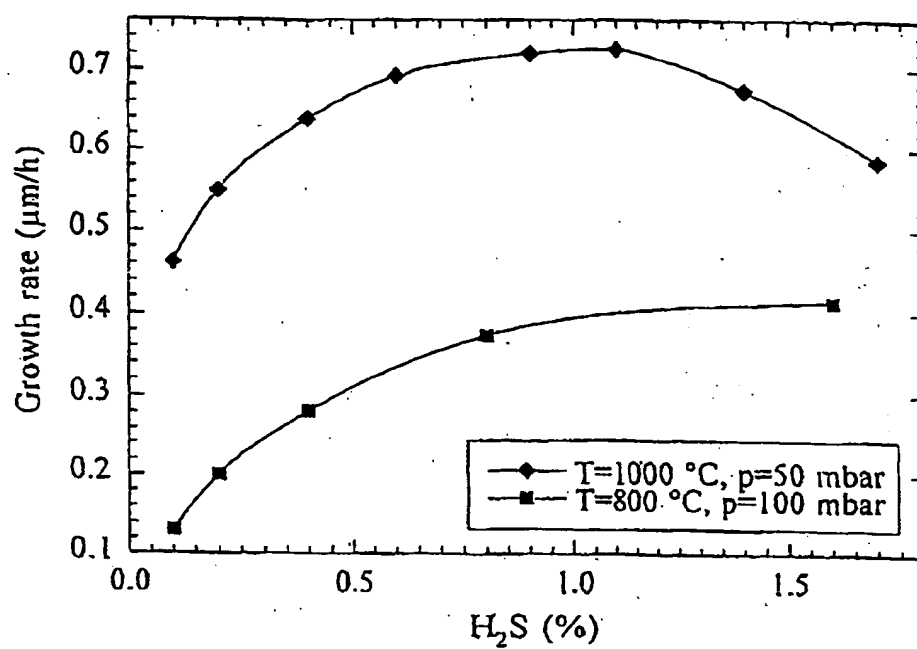
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EUROPEAN SEARCH REPORT

Application Number
EP 01 85 0020

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 99 27155 A (SANDVIK AB) 3 June 1999 (1999-06-03) * example 1 *	1-3, 6, 7, 13, 14	C23C16/40
X	HIROHISA IISUKA ET AL: "GROWTH OF SINGLE CRYSTALLINE -AL2O3 LAYERS ON SILICON BY METALORGANIC MOLECULAR BEAM EPITAXY" APPLIED PHYSICS LETTERS, US, AMERICAN INSTITUTE OF PHYSICS, NEW YORK, vol. 61, no. 25, 21 December 1992 (1992-12-21), pages 2978-2980, XP000331333 ISSN: 0003-6951 * the whole document *	1, 2, 8	
X	YOM S S ET AL: "GROWTH OF Y-AL2O3 THIN FILMS ON SILICON BY LOW PRESSURE METAL-ORGANIC CHEMICAL VAPOUR DEPOSITION" THIN SOLID FILMS, CH, ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 213, no. 1, 29 May 1992 (1992-05-29), pages 72-75, XP000360243 ISSN: 0040-6090 * paragraphs '0002!', '0003!' *	1, 2	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C23C
X	US 5 587 233 A (TABERSKY RALF ET AL) 24 December 1996 (1996-12-24) * column 2, line 38 - column 4, line 13 *	1, 2	
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 08, 30 June 1998 (1998-06-30) & JP 10 068076 A (MITSUBISHI MATERIALS CORP), 10 March 1998 (1998-03-10) * abstract *	1-20	
-/--			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 May 2001	Examiner Ekhult, H
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/92 (P04001)



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Application Number
EP 01 85 0020

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 686 707 A (MITSUBISHI MATERIALS CORP) 13 December 1995 (1995-12-13) * page 3, line 44 - page 4, line 57; table 5 *	1-20	
A	UEKI MITSUO ET AL: "CVD coating of alumina film on WC-betast-Co cemented carbide by using hydrogen sulphide contained atmosphere" J JPN SOC POWDER POWDER METALL; JOURNAL OF THE JAPAN SOCIETY OF POWDER AND POWDER METALLURGY JUN 1994 PUBL BY FUNTAI FUNMATSU YAKIN KYOKAI, KYOTO, JPN, vol. 41, no. 6, June 1994 (1994-06), pages 727-731, XP001004495 * figure 1 *	15-18	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 May 2001	Examiner Ekhult, H
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 85 0020

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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23-05-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9927155 A	03-06-1999	BR 9815043 A	03-10-2000
		CN 1280632 T	17-01-2001
		EP 1034319 A	13-09-2000
		PL 340696 A	26-02-2001
		SE 9704387 A	27-05-1999
		US 6139921 A	31-10-2000
US 5587233 A	24-12-1996	DE 4209975 A	30-09-1993
		AT 155176 T	15-07-1997
		WO 9320257 A	14-10-1993
		DE 59306887 D	14-08-1997
		EP 0632850 A	11-01-1995
		JP 7505442 T	15-06-1995
JP 10068076 A	10-03-1998	NONE	
EP 0686707 A	13-12-1995	JP 2746036 B	28-04-1998
		JP 6190605 A	12-07-1994

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82